## Chapter 11

# CROSSLINKING OF POLYMERS IN RADIATION PROCESSING

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## 1. INTRODUCTION

The first significant industrial use of radiation processing was implemented in the late 1950s, shortly after the discovery of the crosslinking of olefin polymers using ionizing radiation [1, 2]. The practical applications for radiation processing have since grown. Now this process technology is used to manufacture many articles, *e.g.* heat shrinkable tubing and tapes, encapsulations for industrial products, polyolefin foams, *etc*. [3]. The process is widely used in the wire and cable industry to crosslink the insulation and jacketing, with some formulations able to suppress flame propagation, and, being crosslinked, demonstrating increased abrasion resistance and resistance to fluids. Radiation crosslinking of polymeric pipes for water distribution is another product area. Controlled radiation partial crosslinking of the automobile tire plies enhances the dimensional stability of cord placement and reduces material consumption. In medical device area, radiation processing is used to manufacture hydrogels and to modify ultra-high molecular weight polyethylene (UHMWPE) for implants.

Radiation processing is supported by the continued progress in electron beam (EB) accelerator development [4, 5]. A variety of electron beam parameters, such as energy and power, scan width, *etc*., broadens the range of applications. High power accelerators, up to 700 kW, increase the output rate and make the radiation processing cost-effective and competitive with chemical processing [6, 7]. Additionally, irradiated products require neither extra additives nor thermal treatment. These benefits together with low power demand make radiation process a green technology [8, 9].

The practical aspects of radiation crosslinking demonstrate many product benefits [10-12]. The generation of intermolecular bonds between polymeric chains improves various product features, such as: mechanical properties, resistance to corrosive substances, thermal stability, processability, *etc*. Radiation processing can lead to an improvement in product quality and usefulness.

In the summary the innovative applications and trends in radiation technologies are discussed.

## 2. RADIATION PROCESSING IN INDUSTRY AND MEDICAL APPLICATIONS

### 2.1. ELECTRICAL WIRE AND CABLE

In January 1957, Paul Cook founded Raytherm Wire and Cable to take advantage of electron beam induced crosslinking of polyethylene (PE) [13]. Since then, the wire and cable industry has continued to adopt this type of production. The growing demand for crosslinked products stems from their higher quality compared to standard cables and their improved capability to withstand degrading environments [14, 15]. The uses of crosslinked wire and cable are found in various industries, such as: aerospace, automotive, railway, miniaturized electronic equipment and even solar panels.

A key challenge was the development of a non-toxic, low smoke, halogen free insulation and jacketing formulation [16, 17]. Radiation crosslinked wire and cable jacketing is thinner and lighter than competitive materials and, thus, occupies smaller space which is needed in cars, planes and other means of transport. Additionally, the crosslinked, three-dimensional polymer structure does not allow the polymer to melt at elevated temperatures which supports flame propagation resistance.

The composition of wire and cable jacketing varies and uses a wide range of polymers: polyolefins, as polyethylene (PE), blends of PE, ethylene-propylene rubber (EPR) or ethylene-propylene-diene modified elastomers (EPDM), ethylene-vinyl acetate copolymers (EVA), chlorosulfonated polyethylene (CSPE), poly(vinylidene fluoride) (PVDF), and ethylene tetrafluoroethylene (ETFE). The second major component is a flame retardant usually in the form of aluminum hydroxide ($Al(OH)_3$) or magnesium hydroxide ($Mg(OH)_2$). There are also many other additives: antioxidants, plasticizers, lubricants, colorants, stabilizers, inorganic fillers, zinc oxide, *etc*.

During irradiation, the interfacial effects between the conductor made of copper or aluminum and the insulation should be considered since:

- Irradiation is usually accompanied by some low molecular weight gaseous by-products, such as hydrogen in the case of polyethylene. If not diffused through the jacketing, the released molecules could disrupt the adhesion

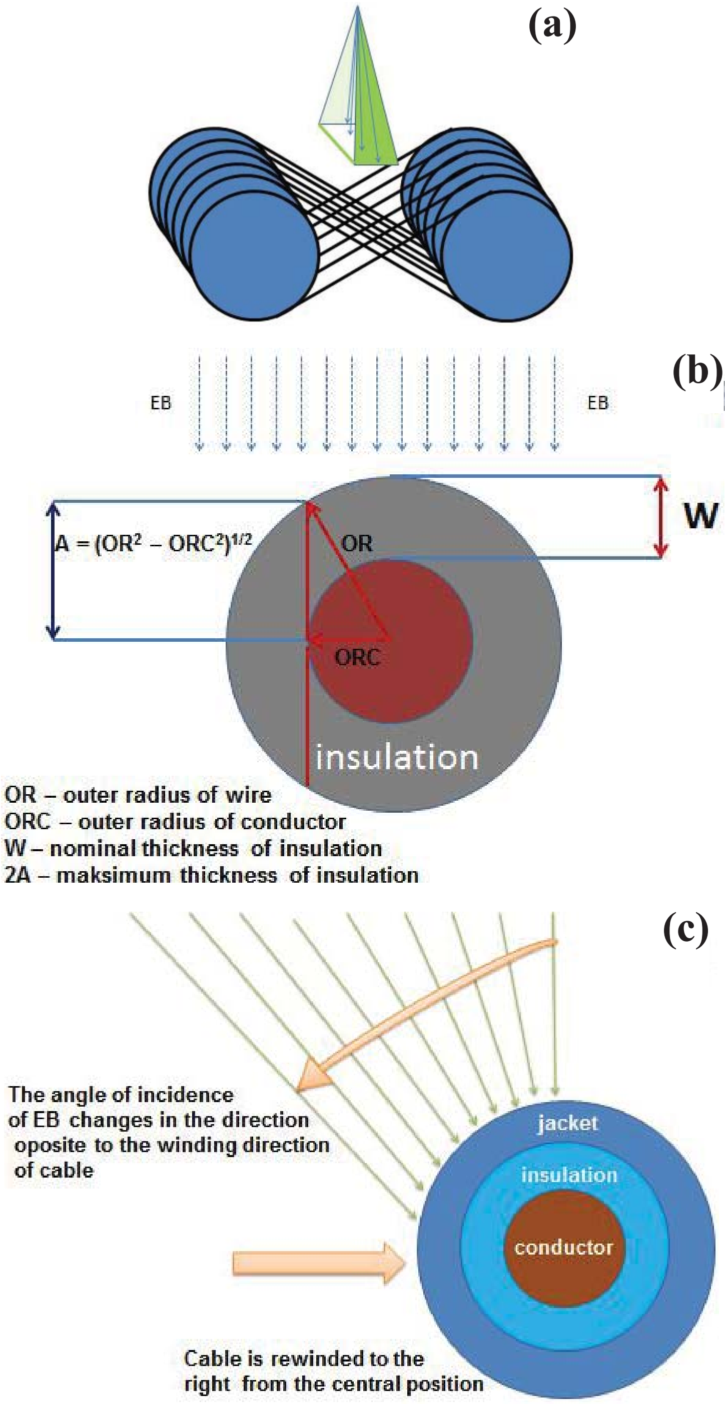

Fig.1. (a) Scheme of figure eight arrangement of under beam facility for radiation processing of cables. (b) Cross-section of wire illustrating penetration of EB by thickness of insulation varying in the range of W-2A. (c) Quasi multi-sided crosslinking during under beam cable transportation.

between the polymer and the conductor, thus impairing the functionality of the wire.

- Since the specific heat of metals is much lower than that of polymers, the heat generated as a result of radiation deposition is transferred from the metal conductor to the polymeric insulation what might undermine the integrity of the insulation.
- Some metals, particularly copper, are very efficient catalysts for redox reactions. In contact with polymeric insulation, such metals can prompt oxidative degradation by stimulating decomposition of peroxide structures and subsequent radical induced processes.

These adverse effects can be eliminated by controlling the parameters of the electron beam and by suitable cable under beam transport systems and, if needed, supplemented with a cooling system.

Important parameters in characterizing the appropriateness of the radiation crosslinking process are the dose and the homogeneity of dose distribution [18, 19]. The circumferential average dose distribution measured by gel fraction for multiple pass irradiation arranged in a figure eight configuration, as shown in Fig.1a, usually provides sufficient dose homogeneity. The uniform dose distribution results from the continuous change in the EB angle of incidence toward the wire or cable. Using an appropriate under beam handling system, as shown in Fig.1a, the wire or cable jacketing is exposed to EB from all sides as the angle of incidence varies continuously from a central to an extreme left/right side (Fig.1c). As shown in Fig.1b, for wire and cable, the electron beam voltage must be chosen such that the beam penetrates though half the cord length (A) of the maximum insulation cord thickness (2A), not just though the thickness of insulation (W). This and the gradual rotation of the wire or cable in an under beam system as shown in Fig.1a will assure uniform dose distribution.

Depending upon the cable thickness and stiffness, and on the EB voltage, under beam facilities can be arranged in one-, two-, or four-sided irradiation configurations [20]. The process technology is tailored to the cable geometry and its flexibility, the absorbed dose and its homogeneity, and electron beam parameters such as voltage.

### 2.2. SELF-REGULATING HEATERS

Another important application of radiation processing is its use in the manufacture of self-regulating or auto-therming cables which generate heat only if the temperature decreases below a specified level [21]. This is based on the positive temperature coefficient (PTC) of radiation crosslinked polymer compositions. If a semicrystalline polymer, such as polyethylene, is appropriately filled with a conductive carbon black (CB) and radiation crosslinked, it will conduct current and act as a resistor between two parallel conductors. As a resistor, the electrically conductive material will generate heat until it reaches the melt transition of the semicrystalline polymer. At that temperature, the crystalline structure “melts” but the material does not become mobile or fluid since it is crosslinked. However, the electrical connectivity amongst the conductive carbon black particles no longer exists and the softened polymer then becomes an insulator, stopping current flow between the parallel conductors. As the polymer cools, it recrystallizes enabling the conductive carbon particles to reestablish an electrical current flow between the conductors and again acts as a resistive heating element. The temperature at which this happens is controlled by the melt transition of the selected polymer, typically a polyethylene or ethylene copolymer. Because conductive carbon black can influence some mechanical properties of the composition, such as flexibility, it is desireable to minimize its concentration. This specific concentration is the percolation threshold, *i.e.* the minimum content of CB allowing for current flow [22]. Conductive nanoparticles, which can form micro-sized aggregates, could be used as the electrically conductive additive.

Self-regulating cables or pieces are often constructed from two parallel copper conductors covered with a semicrystalline polymer formulated with conductive carbon black at a concentration exceeding the percolation threshold. A rise in temperature above the melt transition ($T_m$) of the crystalline phase results in an increase in polymer volume due to the conversion of ordered domains into a disordered melted phase. This disrupts conductive pathways, which cause an increase in resistivity of several orders of magnitude, and results in the cessation of current flow and of resistive heating. These changes are then

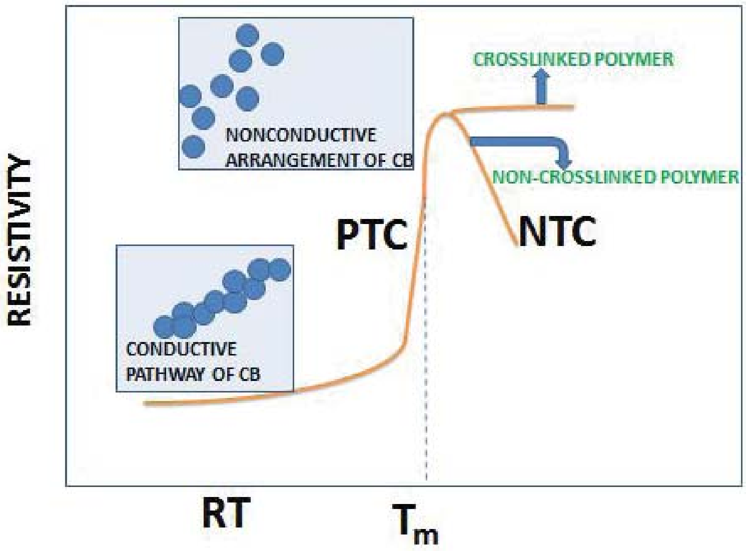

Fig.2. Resistivity as a function of temperature for semicrystalline polymer and CB composite.

followed by a negative temperature coefficient (NTC) when resistivity decreases with temperature increase. Above the polymer's melt transition, there is a CB discontinuity with no current being conducted through the formulated polymer.

The PTC materials require crosslinking. The intermolecular bonding between polymer segments enables the melt-crystallization melt-recrystallization cycles to be repeated. Additionally, the three dimensional polymer network enhances the PTC intensity and reduces the NTC effect, as shown in Fig.2.

PTC devices have to demonstrate the following features:

- Up to a specified temperature, the resistivity ought to be low enough to assure conductivity and consequently resistance heat generation at a desired level.
- High PTC intensity (at least three orders of magnitude) is needed in order to abruptly trigger sufficient resistivity at an elevated temperature ($T_m$).
- No NTC effect which can disrupt the turning on/off of resistive heating.
- Reproducibility and stability which are supported by radiation crosslinking.
- Low CB content at percolation threshold to assure adequate flexibility.

Under these conditions, at low temperature many conductive pathways correspond to the high power output, whereas at high temperature the termination of heat emission stems from a lack of the conductive pathways.

PTC heating products in the form of tapes or cables were patented from the mid-1970s (*e.g.* [23-25]). Wound around pipes they can be used as heating elements that protect transported fluid from solidification or decrease in viscosity of a fluid at low temperatures. PTC heaters might be also incorporated into shrinkable tapes or tubing (see Section 2.3) in order to induce heat shrinking and/or to activate a hot-melt adhesive [26].

The PTC effect is used in many applications, such as resettable fuses which protect electronic devices against overcurrent flow and overheating in computers, telecommunication equipment, rechargeable batteries, power supplies, *etc*. Other applications involve self-regulating heating cables for maintaining selected temperatures of floor heating systems, for the defrosting water pipes, for the snow clearance of roofs and gutters, for the temperature maintenance of hot water pipes.

Radiation crosslinked PTC cables are now being developed for a wide range of temperatures depending on user demand.

## 2.3. SHAPE MEMORY PRODUCTS

Heat shrinkable tubing and tapes are sometimes called shape memory products. Upon heating, they recover to an initial dimension. Heat shrinkable tubing protects connections and terminals in electrical systems against harsh environmental conditions. The tight sealing of the tubing around connectors and terminals keeps out humidity and dust. Heat shrinkable tubing is also used in medical devices, such as catheters or cardiovascular stents to reduce their diameter and minimize invasive surgery. Usually tubing contracts in diameter whereas shrinkable tapes contract in their length.

The manufacture of heat shrinkable products relies on the proper selection of raw materials and formulations to attain a desired set of properties. These formulations are then extruded and the extruded product is radiation crosslinked to create a three-dimensional network between macromolecules. The crosslinked, extruded products are then heated to a temperature above polymer melting transition and expanded. Tubing is expanded in diameter and tapes in length. In this form, the products are cooled to ambient temperature in order for the base polymer to recrystallize and to fix the marketed-shape. In such a state, heat will then be needed to decrystallize the polymer and allow elastic forces to shrink the product around an item [27, 28].

When heat shrinkable tubing or tape is used, reheating above the melt transition of the base polymer is needed to initiate shrinkage and recovery, *i.e.* to achieve the dimensions before expanding. The stages of the production processes are illustrated in Fig.3.

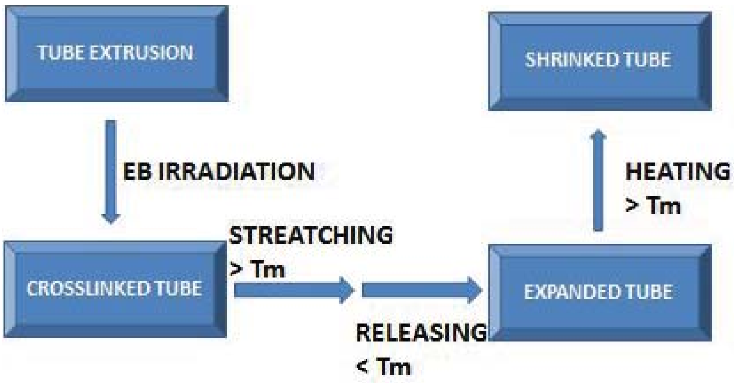

Fig.3. Production of heat shrinkable tubing. $T_m$ – melt transition temperature of polymer.

In the shape memory cycle, shown in Fig.4, there are four distinctive stages [29]:

- heating to a temperature above the base polymer's melt transition,
- expanding or stretching under pressure or force to a shape at which the product will be marketed,
- cooling to room temperature (RT),
- shape recovery after heating above the $T_m$ of the base polymer.

For heat shrinkable products, crosslinking is needed since expansion occurs above the melt transition of a thermoplastic and the product must maintain the stretched form for long period of time at ambient temperature. If polymers did have not intermolecular chemical bonds (crosslinks), they could not be ex-

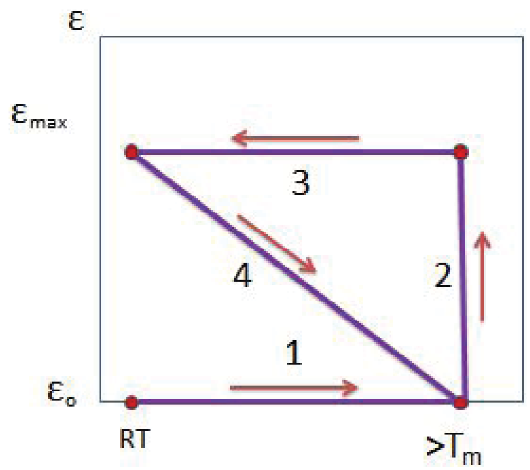

Fig.4. The shape memory cycle presented as a relationship between temperature and strain.

panded above their melt transitions. Shrinking stress increases with increased crosslinked density. The stretch ratio is defined as a ratio between the expanded and initial dimensions. To have maximum shrinkage recovery, the product heating temperature (4. stage in Fig.4) has to be above $T_m$, otherwise there will be only partially recovered.

Hot-melt adhesive coated heat shrinkable tapes can be applied to pre-insulated pipe systems, which upon heating melts the adhesive and shrinks the tape to form an impervious tight seal.

## 2.4. RADIATION LONG-CHAIN BRANCHING AND THE CROSSLINKING OF POLYMERIC FILMS

The processability of polymers is determined by their molecular structure. Linear, one-dimensional polymer backbones (Fig.5A) can exhibit poor processability. Highly crosslinked polymers will not melt and they cannot be extruded or molded (Fig.5C). Branched polymers (Fig.5B) and lightly crosslinked ones can be melt processed. When irradiated with small doses (10 kGy or less), the irradiation induces effects in polyolefins which cannot be estimated by gel fraction measurements since the polymer can be dissolved. This kind of modification is sometimes recognized as a long-chain branching (LCB) which can improve rheological properties, particularly melt strength, and the processability of the polymer. It must be then taken into account that upon branching, the melt strength increases and the crystallinity decreases. The side chains are considered as LCB if their chain length exceeds 40 carbon atoms.

The commercial applications of gel-free irradiated polypropylene (PP) was implemented in 1990s and of polyethylenes much earlier [30, 31]. Among

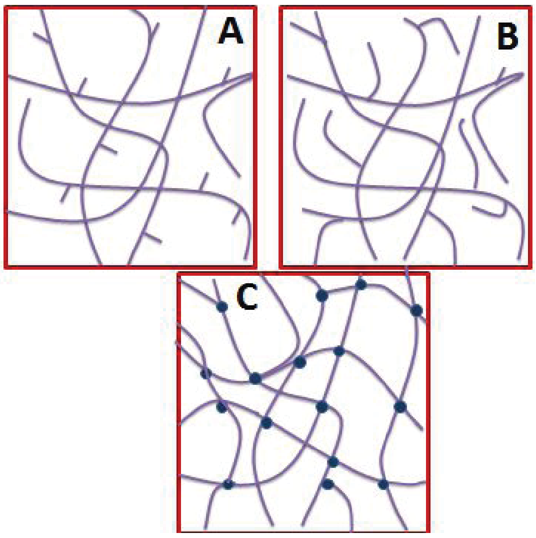

Fig.5. Various structures of polymers: (A) chains with many short branches, (B) long-chain branched polymer, (C) high density crosslinked polymer.

various types of polyethylenes, low density polyethylene (LDPE) itself demonstrates good melt strength resulting from the presence of long side chains. High density polyethylene (HDPE) and linear low density polyethylene (LLDPE) do not have such branching. It was thought that low dose, gel free irradiation would enhance LCB and improve processability. Such low dose irradiation of polyethylenes and of polypropylenes to modify melt toughness has not been sustained in commercial practice.

The manufacture of irradiated blown films is one of the most common irradiation processes in use on a worldwide basis. Such films are manufactured by the extrusion of the molten polymers followed by irradiation and then blowing, cooling and winding of the finished film product [32]. In the first stage, the molten material is extruded by a circular die in the form of tube which is then irradiated. Subsequently the irradiated tube is expanded radially by introducing air to form a bubble up to several times larger in diameter than that of the extrusion die. The crosslinked bubble is also drawn by a pulling in the direction of extrusion. In the final stage of the production line, the stretched, crosslinked film is wound onto a drum. These films are heat recoverable as are tubings and tapes discussed above.

In many cases films are constructed from three to five layers and are produced by coextrusion. If the film layers do not bond together, they would delaminate. To overcome the problem, thin layers of polymers having adhesive properties, known as tie layers, are used in between the functional film layers. Thus, more than 5 layers are then required. Barrier films are produced with blown coextrusion technology where different resins are extruded and brought together through the die. The multi-layer extrudate is then irradiated and blown up into a bubble. When the bubble is cooled sufficiently, it is collapsed between rollers and collected on a roller.

The expanded bubble can be anisotropic and show two distinctly different axes as:

- the machine direction (MD),
- the transverse direction (TD).

Variations in tear resistance can be a consequence of the crystalline lamellar structure formed during film blowing. HDPE films have a row-nucleated fibrillar morphology, very loosely interconnected in the crosswise (TD) direction. In this case, MD tensile is greater than TD tensile, and the tendency to tear is opposite. On the other hand, for LDPE having long-chain branches, the preferential morphology is a lamellar structure interconnected by the separated bounds. This arrangement results in higher tear resistance in MD than in the TD direction. LLDPE tear properties are relatively balanced due to less oriented topology/morphology.

## 2.5. RADIATION USE IN THE PRODUCTION OF FOAMS

Foam technology has been developing since 1930s when blowing agents were used in the polymer processing. Polymer foams consist of two phases: a polymeric matrix and entrapped, well dispersed cells generated by blowing agents. Foams have several advantages: low density, insulating capability, energy absorption, *etc*. These make foams a desired product in many applications such as packaging, floating materials, paddings, shields for reducing noise, shoes, *etc*. [26]. Foam density varies across a wide range from several kg/m$^3$ to near thousands kg/m$^3$. The average size of the micelles determines their number in cm$^3$ which might reach $10^6$ for conventional foams and above $10^9$ for microcellular foams.

Various polymers are used in foam technology, among which the most widely used are polyurethanes, polystyrene, poly(vinyl chloride) and polyolefins [33]. The last group of materials, PE and PP, are low-cost polymers of well-balanced properties. When using radiation processing in foam manufacture, the production process consists of (i) compounding the polymer and blowing agent, (ii) extruding the compound into sheets, (iii) radiation crosslinking the sheet, and (iv) foaming the crosslinked sheet with heat provided by moving platens [34].

Foams can be crosslinked or non-crosslinked and can be open or closed cell [35]. In terms of mechanical properties, foams can be classified as hard (made from PP or PE) or soft (made from EVA copolymers). The amount of blowing agent and the crosslinked density determine the final foam structure. The advantage of using radiation processing is that one has a more robust process in that blowing agents will not be activated until after crosslinking which enables control of foam density and micelle size.

The structure of polyolefin foams is determined by the concentration of blowing agent mixed into the polymer. Micelle nucleation is trigged when the blowing agent thermally decomposes to release gases, such as nitrogen or carbon dioxide. Final foam density and morphology depends on the amount of gases released and on the crosslinked density of the polymer. The extrudate viscosity might be reduced since blowing agents can demonstrate a plasticizing effect.

Polymer crosslinked density is a factor influencing the growth of the foam structure by restricting cell coalescence under pressure of the expanded gas. Crosslinking of the polymer decreases the possibilities of cell wall rupture during expansion. The crosslinking density determines the micelle dimensions and controls their growth. During foaming the cell walls get thinner due to continuous stretching. Thus, the strength of crosslinked polymer must be sufficient to maintain bubbles inside the foaming material. It is well known that low and medium crosslinked density preserves some elastic features of polymer, whereas high crosslinked density can make a polymer more rigid.

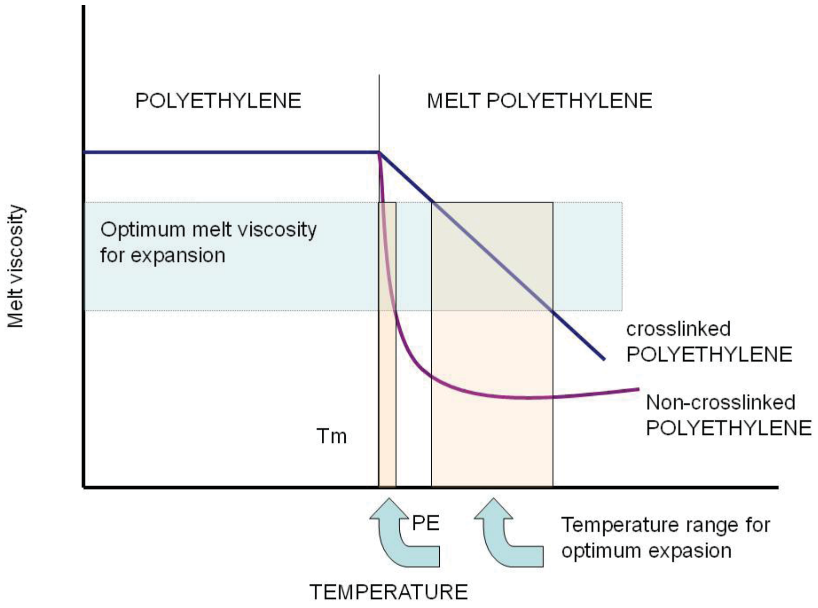

Fig.6. Influence of polyethylene crosslinking on the optimal range of processing temperature during foam production.

The modification of properties due to crosslinking extends the range of temperatures in which a foam might be formed. As seen in Fig.6, for a non--crosslinked polymer, the temperature range for foaming is very limited.

In polyolefin foam production, radiation processing permits a wider temperature range for expansion conditions. This results in the manufacture of low density foam with physical properties suitable for use in medical devices, automotive applications, sporting equipment, *etc*.

## 2.6. RADIAL TIRES

The manufacturers of radial tires use electron beam processing to partially crosslink plies that will be molded and cured into the final tire [36]. These radiation partially crosslinked rubbers allow tire cords to be positioned and held in place during the final molding process.

Rubber plies used in constructing a tire can deform during assembly if only a conventional vulcanization process is used. This can lead to an uneven distribution of the components and to reinforcing cords being dislocated. In order to avoid such undesired consequences in straight forward thermal curing, the rubber plies or belts are thickened. An alternative is to partially crosslink, usually in the range of 30-50 kGy, the rubber plies. This introduces dimensional stability, improves balance and allows the manufacturer to reduce the amount of material used in the tire (Fig.7). With EB processing, there are fewer defects in the tires and a lower consumption of rubber. Many tire companies, including all Japanese ones, routinely use EB crosslinking of tire plies as a high speed, tightly controlled pre-vulcanization process.

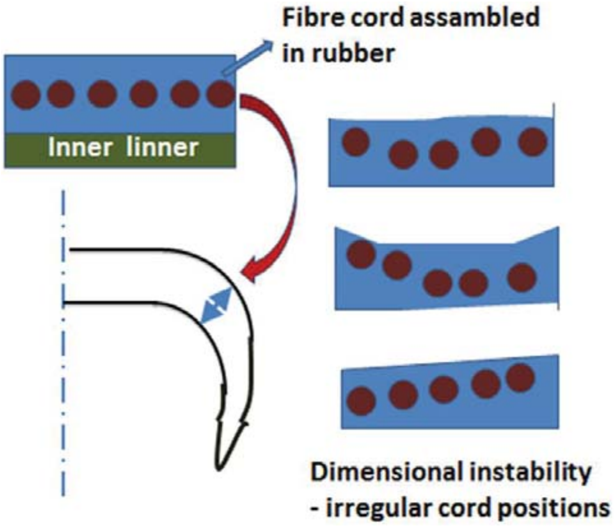

Fig.7. Dimensional instability of non-crosslinked tire plies.

## 2.7. RADIATION CROSSLINKING OF MEDICAL DEVICES

The acceptance of medical devices is a multistage complex process in which many factors have to be taken into account: clinical issues, structural requirements, material selection, processing aspects, *etc*. Such a strategy is also necessary in the development of implants. The acetabular cup for total hip replacements and the patellar components for total knee replacements are routinely manufactured from ultra-high molecular weight polyethylene (UHMWPE). Every year the forces of 4 to 7 times greater than body weight of patients are transferred millions times to the implant. Clinical experience indicates that in some cases 6 to 8 years after implantation the components fail due to oxidative degradation of polyethylene, facilitated by the surrounding body fluids. With time, small debris of the polymeric material is peeled away what is defined as progressive wearing. This wear process, together with implant fatigue, may cause pain and, ultimately, loosening of the prosthesis.

The wear resistance of UHMWPE might be enhanced by radiation crosslinking [37, 38]. This substantially improves material strength and prolongs implant lifetime. The final effects strongly depend on the initial UHMWPE structure. Alkyl radicals are generated by ionizing radiation in both phases, amorphous and crystalline, of the polymer during irradiation. In the disordered, amorphous domains, due to local conformational movements, the radicals recombine forming a three-dimensional crosslinked network. On the other hand, in the crystalline regions, radical centers are localized creating so-called residual radicals which are a relatively long-lived species. These radicals within the crystalline domains are stable and, in long term, are responsible for the oxidative degradation of the polymer [39, 40]. Several scenarios have been proposed to eliminate this drawback.

Heating UHMWPE at temperatures around its melting point is the most commonly used treatment to decay residual radicals [41, 42]. Thermally stimulated molecular movements promote the termination of radicals, leading to the interruption of chain sustaining radical formation. On the other hand, the thermal treatment decreases mechanical strength since upon cooling the crystalline phase of the crosslinked polymer diminishes.

In order to avoid reduction of crystallinity during post-irradiation heating, another approach has been proposed involving the doping of the radiation treated polyethylene with a biocompatible antioxidant in the form α-tocopherol (vitamin E) [43, 44]. The introduction of the vitamin significantly decreases the population of stable radicals but simultaneously increases the dose required to reach the assumed level of crosslinking.

Radical quenching under high pressure is another treatment that has been considered. At elevated temperature and high pressure, UHMWPE forms hexagonal crystals which have a tendency to form large ordered structures. Overall crystallinity increases presumably improving mechanical strength of the material.

Gradient crosslinking of UHMWPE using irradiation in molten state is a promising option that might overcome the drawbacks related to the residual radical effects. The liners are irradiated at temperatures of about 140°C with electron beam of energy below 2 MeV. The limited penetration of the accelerated electrons results in a considerable and gradual decrease in crosslinked density with the depth. Under such conditions, the implant interior remains unchanged, whereas the surface, which ought to withstand heavy tribological load, is protected by crosslinking.

Experimental results have shown inhomogeneous post-irradiation oxidation with severe subsurface embrittlement and cracking. The distribution of oxidation products is estimated by infrared determination of the oxidation index. This parameter is usually calculated as a ratio between the peak area of the carbonyl group (C=O) absorption band at 1717 $cm^{-1}$ and the area of the methylene group reference band at 1370 $cm^{-1}$.

Generally, radiation crosslinking of the amorphous phase increases wear resistance of the implant. On the other hand, the enhanced interior crystallinity restrains the fatigue of the material [45]. Thus, a properly optimized microstructure is the key for providing UHMWPE materials with resistance to both wear and fatigue [46].

Recently, the following procedure has been proposed for manufacture UHMWPE implants: UHMWPE is blended with 0.1% α-tocopherol powder and then compression molded in the form of bars. The bars are radiation crosslinked with an elevated dose to overcome the scavenging ability of the vitamin. The irradiated polymer is then heated and compressed to promote free radical decay. The final implant product is machined from these irradiated bars, packed and sterilized with ethylene oxide.

## 3. EMERGING APPLICATIONS OF RADIATION PROCESSING

The development of cost-effective and diverse accelerators provides electron beams of various energies and powers, and stimulates progress in radiation processing that may offer a new generation of products with enhanced quality [47]. Radiation processing is of growing importance in medical devices, in aerospace applications, in the polymer industry and in agriculture. New trends for electron beam applications appear since EB processing substantially enhances the commercial value products.

There are many new areas that can in the near future generate a growing demand for electron accelerators.

**Innovative high-performance carbon fiber composites**

The manufacture of the carbon fiber reinforced polymer composites with exceptional resistance to harsh or aggressive environments might be performed through the use of ionizing radiation. Specifically oriented reinforcements in a form of carbon fiber layers allow for the production of materials with anisotropic features. Such carbon fiber composites can be made using radiation processing. These types of high-performance materials are recommended for use in space applications, communications or transportation areas.

### Self-healing polymer composites

High energy electron beams may prove to be a convenient way to manufacture lightweight fiber reinforced composites which have high resistance to degrading factors and yet self-healing capacities. The EB technique might contribute to the construction of smart materials capable repairing damages caused by various stresses (elevated temperature, pressure, radiation, mechanical stress) over long periods of time.

A reversible correction of a composite might be performed if it includes a predetermined microencapsulated healing agent that would dispense upon damage (microcracks). Ionizing radiation is an appropriate source of energy both for synthesis of repair formulas and for their introduction into the polymeric matrix. The development of such work is targeted towards the automotive and aerospace industries.

### Conducting nano- and microcomposites as sensors

Strain sensors using conductive polymer nanocomposites have recently been developed. These are promising materials for the construction of electromechanical sensors only if the conducting filler in a polymeric matrix reaches a percolation threshold. An innovative approach is needed to develop a reversible sensor using crosslinked flexible polymers of low hysteresis.

Strain sensing devices are being explored using EB crosslinking of conducting nanocomposites to improve their operation and durability. Radiation processing is also considered important for the production of current protection devices, shielding systems, sensors for security systems, *etc*.

### Top-down and bottom-up synthesis of nanomaterials

EB processed nanotechnology opens up new possibilities for the fabrication of nanostructured materials. Ionizing irradiation permits the building of nano-sized structures with strictly defined and uniform geometry from the molecular level up or by a top-down approach when the material is ground or decomposed to the nano-scale.

This technique can be used for the formation of track nanoporous membranes (used also as a template for synthesis of inorganic nanoparticles) and for the generation of metal clusters in zeolites and solutions. Such nanoparticles with a desired functionality can find applications as biosensors or catalysts. Depending on chemical structure, these materials could be able to react or to change their size depending on external stimuli, such as ionic strength, heating, pH, light emission, reactant concentration.

### Radiation technology in medically oriented applications

Nanogels are used in biomedical applications as drug delivery systems, as cell markers, as replacements for biopolymers, as structures for the immobilization of biologically active molecules, *etc*. An uncomplicated radiation process can initiate the synthesis and crosslinking of high-purity micro- or nanospheres.

The important advantage of this technique is that the resulting products can play a role as carriers for drugs, antibodies, enzymes, *etc*. In future the technology might be adapted for manufacturing biomedical microdevices, vectors for genes or other biologically active substances and their controlled release. The other attractive potential application involves scaffolds for tissue engineering, cartilages, artificial blood vessels, *etc*., or structures constructed from ligand binding nanoparticle as target receptors, which properties might be tailored by ionizing radiation treatment.

**New crosslinkable polymers**

The increase in heat resistance results in greater value added polymers. Thus, crosslinking in many cases expands the profit margins and the use of polymers. New substances might be developed which under selected conditions might be responsive to ionizing radiation and form intermolecular bonds or crosslinks. Radiation crosslinking of engineering polymers is difficult due to the presence of aromatic rings that disperse deposited energy. On the other hand, some polymers might be crosslinked only under specific conditions, *e.g.* poly(tetrafluoroethylene) (PTFE) is crosslinkable in near its melt transition. It has been found recently that radiation degraded polymers in paste-like form might be susceptible to radiation crosslinking.

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